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## (54) Process for the removal of contaminants

(57) A process for the removal of contaminants from a material, for example PCB's, from for example sludge or slurries is described, the process comprising contacting the sludge or slurry with a C<sub>1</sub> - C<sub>4</sub> fluorinated hydrocarbon, especially tetrafluoroethane, and separating the solvent charged with contaminants from the material.

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PROCESS FOR THE REMOVAL OF CONTAMINANTS

This invention relates to the removal of contaminants and, in particular, but not exclusively, to the removal of 5 chlorinated hydrocarbons from a material contaminated therewith.

Poly chlorinated biphenyls (PCB) is a generic term used to describe a class of over 209 chemical substances 10 all of which have similar characteristics. They are considered to be extremely harmful to the environment and potentially dangerous to human and animal life. They are extremely widely distributed throughout the environment. They can be precursors of dioxins. Every capacitor 15 associated with a fluorescent light fitting, which is over 25 years old probably contains PCB.

These chemicals have been available since the 1930's and were produced in the UK after 1954, though their 20 production was prohibited in 1976.

The very advantageous properties which hitherto rendered them useful in the electrical industry are now perceived to be potentially catastrophic. They are very 25 highly persistent in the environment being chemically inert, durable and oil soluble, three properties originally considered to be to their commercial and practical advantage. These properties have now led to the realisation that they are very hazardous and this has led 30 to vigorous moves to eliminate them from the planet. These actions were begun as long ago as 1976.

PCBs have been shown to enter the food chain and render some animals, which ingest them, incapable of 35 breeding whilst causing others to produce young with

serious birth defects. They also suppress or damage the immune system leading to premature death.

Apart from their occurrence in minute quantities in animal flesh (particularly skeletal fats) as a result of their presence in the food chain, PCBs are also to be found in large abundance in soils (where they have been disposed of as solutions in and with petroleum based oils or as a discharge from transformers and other heavy electrical equipment during demolition), muds (where the soils have become part of a river-bed or water-course or harbour sludge), adhering to fragmented scrap resulting from the break up of electrical plants and in many other undesirable locations.

Methods accepted for the disposal of PCBs include : specialist oxidative high temperature incineration where destruction and removal efficiencies (DREs) of 99.9999% are reported; chemical and electrochemical methods such as de-chlorination; and, when found in fuel-oils, a high temperature treatment ( $> 1400$  deg C) in cement kilns for a long period of time ( $> 3$  minutes) in an alkaline environment which destroys the PCBs without their re-combination to form dioxins.

Unfortunately, the problem of disposal of large tonnages of such contaminated waste will almost certainly outstrip the capacity of these various mechanisms of destruction to keep up with the demand for their elimination from the environment. Furthermore, these techniques can only readily be applied to the destruction of contaminated oils.

Such techniques are expensive and in many cases are not suited to disposal of much of the contamination, as in

the case where PCB waste has a substantial water or mineral content e.g. in the cases of sands, soils, muds, slurries and sludges.

5 Part of the disadvantage of the current disposal method is the huge volume of waste of which it is necessary to dispose.

10 One of the objects of the invention is to address the above problems.

According to the present invention there is provided a process for the extraction of at least one contaminant from a material contaminated therewith comprising the 15 steps of :-

- (a) contacting the material with a solvent comprising C<sub>1</sub>-C<sub>4</sub> fluorinated hydrocarbon so as to charge the solvent with the contaminant and
- 20 (b) separating the charged solvent from the remainder of the material.

The preferred fluorinated hydrocarbons described not 25 only display highly selective solvent properties (being able to selectively remove, for instance, PCBs from a variety of "matrices") but also have the physical properties of very low boiling point which provides for their complete recovery and re-cycling, thereby permitting 30 any dissolved PCBs to be left behind whilst the fluorinated hydrocarbon can be continuously re-cycled without significant emissions and hence imposing no threat to or cost/penalty onto the environment.

Furthermore, preferred hydrofluorocarbons are themselves non-toxic, non-flammable, and do not appear to have undesirable side effects, even if they are accidentally emitted into the environment.

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Said contaminant is preferably an organic contaminant, more preferably, a synthetic organic contaminant. Said contaminant may be a halogenated, for example a chlorinated hydrocarbon. Said contaminant may be 10 polyhalogenated, for example polychlorinated and have more than 2, suitably more than 3, especially more than 4 halogen atoms. Said contaminant may be an aromatic, especially a polycyclic aromatic compound. Preferably, said contaminant includes a phenyl moiety, more preferably a 15 polyphenyl moiety. Said contaminant may be toxic.

✓ 20

Said contaminant preferably does not occur naturally in said material. Said contaminant is preferably added either directly or indirectly to the said material as a waste product.

Said material may be a natural matrix.

Said material may optionally contain one or more of 25 soil, mud, slurries, sludge, sand, oil, for example, cellulose based oil (natural or mineral) or water.

30

Said material may be a synthetic or processed material. Said material may optionally be oil based. The C<sub>1</sub>-C<sub>4</sub> fluorinated hydrocarbon may be non-chlorinated. Preferably it comprises one or more carbon, fluorine and hydrogen atoms only. Preferably, said hydrofluorocarbon is a C<sub>1</sub> to C<sub>3</sub>, more preferably, a C<sub>1</sub> to C<sub>2</sub>

hydrofluorocarbon. Especially preferred is a C<sub>2</sub> hydrofluorocarbon.

5 Said hydrofluorocarbon may include up to 10, preferably up to 8, more preferably up to 6, especially up to 4, fluorine atoms.

Said hydrofluorocarbon is preferably aliphatic. It is preferably saturated.

10 Said hydrofluorocarbon may have a boiling point at atmospheric pressure of less than 20°C, preferably less than 10°C, more preferably less than 0°C, especially less than -10°C. The boiling point may be greater than -90°C, 15 preferably greater than -70°C, more preferably greater than -50°C.

20 A preferred hydrofluorocarbon solvent is tetrafluoroethane with 1,1,1,2-tetrafluoroethane being especially preferred.

Said solvent may comprise a solvent mixture of hydrofluorocarbon solvent as described and a co-solvent which may also be, but is preferably not, a 25 hydrofluorocarbon of the type described herein. Said co-solvent is selected to affect the boiling point and/or dissolution properties of the solvent for the contaminant. The boiling point of said co-solvent may be less than 60°C, preferably less than 30°C, more preferably less than 15°C, 30 especially less than 0°C. The boiling point of said co-solvent may be greater than -90°C, preferably greater than -70°C, more preferably greater than -50°C.

35 Said solvent may include one or more co-solvents of the type described.

Preferably, said solvent comprises a major portion of said hydrofluorocarbon and a minor portion of said co-solvent. Preferably, up to 90 wt%, more preferably up to 93 wt%, especially up to 97 wt% of said solvent is 5 comprised by said hydrofluorocarbon. Preferably, at least 50 wt%, more preferably at least 60 wt%, especially at least 70 wt%, more especially at least 80 wt%, most especially at least 85 wt% of said solvent is comprised by said hydrofluorocarbon. The balance is preferably made up 10 of one or more co-solvents as described.

Said co-solvent may be selected from hydrocarbons and ethers. Preferred hydrocarbons have up to six carbon atoms. They may be alicyclic or, preferably, aliphatic. 15 They are preferably alkanes with methane, ethane, propane and butane being preferred. Preferred ethers are dialkylethers, for example, C<sub>1</sub> to C<sub>4</sub> dialkyl ethers, with dimethyl ether being especially preferred.

20 Preferably, the solvent contacted with said material has a lower boiling point than said contaminant.

Preferably, in the method said material and said solvent are intimately mixed prior to step (b).

25 The charged solvent may be collected by decantation. Alternatively, the charged solvent may be collected by sedimentation. Alternatively, the charged solvent may be collected by filtration.

30 Preferably, the solvent is removed from the contaminant by a suitable evaporation technique. Preferably distillation is employed. Said distillation may take place under low vacuum.

The method preferably includes the step of removing said solvent from the remainder of said material, after step (b). Removal of said solvent may be achieved by providing conditions for the evaporation of said solvent.

5 For example, the temperature may be raised, suitably by less than 50°C, preferably less than 40°C, more preferably less than 30°C, and/or the pressure may be reduced to less than ambient pressure.

10 The method may be repeated to effect an increased yield of removed contaminants.

Specific examples of the invention will now be described.

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Example 1

A sample of cotton wool was placed into a small glass tube and a sample of "Araclor" (PCB) in solution in hexane 20 was dispersed on it. The hexane was allowed to evaporate overnight leaving the PCB in intimate contact with the cellulose fibres of the cotton wool.

The entire glass sample tube (containing the cotton 25 wool) was placed into a wide mouthed PET bottle which could be sealed with a removable aerosol valve and filter. 100 grams of 1,1,1,2-tetrafluoroethane (TFE) was introduced into the glass tube and shaken with cotton wool so that the solvent was brought into intimate contact with 30 the cotton wool.

The solvent was then transferred from the PET bottle to a glass "evaporator" bottle and the 1,1,1,2-tetrafluoroethane was completely recovered from both 35 bottles.

An oily residue remained in the glass evaporator bottle and analysis of this residue by chromatographic means confirmed that 98% of the PCB originally applied to the cotton wool was now contained within this residue.

5

Examples 2 and 3

In Example 2, a sheet of aluminium foil and a piece of Whatman filter paper were wound together on a mandrel. 10 A known weight of "Araclor" (PCB) was added to the filter paper in an attempt to reproduce, to some extent, the circumstances within an electrical condenser.

In Example 3, a similar experiment to Example 2 was 15 undertaken wherein aluminium foil was co-wound together with a sheet of heavy industrial gauge insulating paper onto a mandrel. "Araclor" was added to this paper.

Both these samples were placed into a PET bottle (as 20 described in example 1) and brought into intimate contact with 100 grams of 1,1,1,2-tetrafluoroethane.

Transfer of the 1,1,1,2-tetrafluoroethane to separate 25 glass evaporator bottles allowed for the reclamation of all the 1,1,1,2-tetrafluoroethane from all four bottles.

Analysis of the residues inside the two glass bottles showed that 97% and 96% of the "Araclor" had been transferred from the papers to the evaporator bottles for 30 Examples 2 and 3 respectively.

Example 4

A small sample (20 grams) of PCB contaminated cod 35 liver oil was shaken in a PET bottle with 100 grams of a

5 mixture of 1,1,1,2-tetrafluoroethane and 10 wt% of a proprietary hydrocarbon mixture comprising 60% iso-butane and 40% n-butane. Decanting of the solvent which comprised the lower layer of the two phase system into a glass evaporator bottle allowed removal of the solvent and recovery of the residues.

10 A small amount of an oily residue was again observed in the bottom of the glass evaporator bottle when all the solvent had been recovered. This oily residue contained a substantial amount of PCB. Repeating this experiment yielded more PCB. A third extraction revealed that all the PCB had been removed from the cod liver oil.

15 Example 5

20 A sample of harbour sludge believed to be contaminated with PCB which comprised oil soaked sand/soil and water was shaken up repeatedly with 1,1,1,2-tetrafluoroethane containing 10 % w/w of di methyl ether.

25 After separation and evaporation, the glass evaporator bottle contained substantial quantities of a clear yellow mobile oil which contained PCB. Repetition of this experiment three more times increased the total volume of the oil residue in the glass evaporator bottle. This oil was shown to contain substantial amounts of PCB upon chromatographic analysis using high resolution capillary gas chromatography and comparing the results 30 against a known standard mixture of PCBs.

Example 6

35 A sample of fish paste, contaminated with PCB, was shaken with 1,1,1,2-tetrafluoroethane and, after

separation, the solvent was evaporated from the glass evaporator bottle.

5 The oily residue in the evaporator contained substantial amounts of PCB.

Example 7

10 200 grams of transformer oil, a cloudy, yellow, viscous liquid, contaminated with PCB, was shaken repeatedly with 200 gram portions of a mixture 1,1,1,2-tetrafluoroethane containing 10 wt% of a proprietary mixture of 60 part iso-butane and 40 parts n-butane.

15 20 The two layers of the two phase system so formed, were allowed to separate (the solvent being the lower layer) and the solvent was decanted into a glass evaporator bottle. This procedure was repeated twice more and the residues (following removal of the solvent) were pooled. The combined residues comprised a clear, pale yellow, mobile oil with a substantial content of PCB as judged by capillary gas chromatography against a standard Araclor mixture.

25 30 The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

35 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination,

except combinations where at least some of such features and/or steps are mutually exclusive.

5        Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of  
10      a generic series of equivalent or similar features.

15      The invention is not restricted to the details of the foregoing examples. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A process for the extraction of at least one contaminant from a material contaminated therewith  
5 comprising the steps of :-
  - (a) contacting the material with a solvent comprising C<sub>1</sub>-C<sub>4</sub> fluorinated hydrocarbon so as to charge the solvent with the contaminant and
  - 10 (b) separating the charged solvent from the remainder of the material.
2. A process according to Claim 1, wherein said  
15 contaminant is an organic contaminant.
3. A process according to Claim 1 or Claim 2, wherein  
said contaminant is halogenated.
- 20 4. A contaminant according to any preceding claim,  
wherein said contaminant is toxic.
5. A process according to any preceding claim, wherein  
said contaminant does not occur naturally in the said  
25 material.
6. A process according to any preceding claim, wherein  
said material is a natural matrix.
- 30 7. A process according to any preceding claim, wherein  
said material is selected from soil, mud, slurries,  
sludge, sand, oil and water.
- 35 8. A process according to any preceding claim, wherein  
the fluorinated hydrocarbon is non-chlorinated.

9. A process according to any preceding claim, wherein said hydrofluorocarbon is aliphatic.
10. A process according to any preceding claim, wherein 5 said hydrofluorocarbon has a boiling point at atmospheric pressure of less than 20°C.
11. A process according to any preceding claim, wherein 10 said hydrofluorocarbon has a boiling point at atmospheric pressure which is greater than -90°C.
12. A process according to any preceding claim, wherein said hydrofluorocarbon is tetrafluoroethane.
13. A process according to any preceding claim, wherein 15 said solvent comprises a solvent mixture of hydrofluorocarbon solvent and a co-solvent.
14. A process according to Claim 13, wherein the boiling 20 point of said co-solvent is less than 60°C and greater than -90°C.
15. A process according to Claim 13 or Claim 14, wherein 25 said co-solvent is selected from hydrocarbons and ethers.
16. A process substantially as hereinbefore described with reference to the examples.



The  
Patent  
Office

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Application No: GB 9725895.8  
Claims searched: 1-16

Examiner: Alan Kerry  
Date of search: 30 March 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): B1F; B1Q; C1P PP, PW; C5C CDD; C5E ECS, ECV, ESU

Int Cl (Ed.6): A62D 3/00; B01D 11/00, 11/02, 11/04; B08B 3/08; B09C 1/02; C02F 1/26; C11D 7/50; C23G 5/02, 5/028

Other: Online databases: WPI, CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X, P	GB 2308819 A (CARR) - see Claims 1 & 6 and page 2, lines 45-58	1-9
X	GB 2276392 A (DGP) - see Claims 1, 5 & 6	1-12
X	US 5445757 (PENNENTREAU) - see Claim 1	1
X	US 4793931 (STEVENS) - see Claims 1 & 17	1-9
X	US 4483717 (OLMSTED) - see Claims 1 & 2	1 & 2

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.